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BIPOTENTIOMETRY IN ORGANIC REDOX SYSTEMS

**I. OXIDATION OF AROMATIC COMPOUNDS
IN TRIFLUOROACETIC ACID**

by

Harvey W. Yurow

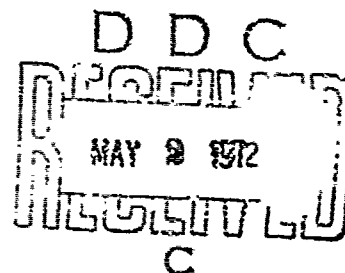
Samuel Sass

April 1972



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| Security Classification | | | DOCUMENT CONTROL DATA - R & D | | |
|--|--|---|--|-----------------------|--|
| (Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified) | | | | | |
| 1. ORIGINATING ACTIVITY (Corporate author) CO, Edgewood Arsenal ATTN: SMUEA-R-CRA Edgewood Arsenal, Maryland 21010 | | | 2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED | | |
| | | | 2b. GROUP NA | | |
| 3. REPORT TITLE BIPOTENTIOMETRY IN ORGANIC REDOX SYSTEMS. I. OXIDATION OF AROMATIC COMPOUNDS IN TRIFLUOROACETIC ACID | | | | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) This was started in October 1969 and completed in June 1970. | | | | | |
| 5. AUTHOR(S) (First name, middle initial, last name) Harvey W. Yurow and Samuel Sass | | | | | |
| 6. REPORT DATE April 1972 | | 7a. TOTAL NO. OF PAGES 15 | | 7b. NO. OF REFS 13 | |
| 8a. CONTRACT OR GRANT NO. | | 9a. ORIGINATOR'S REPORT NUMBER(S) EASP 1200-2 | | | |
| 8b. PROJECT NO. | | | | | |
| c. Task No. 1B562602AD1002 | | 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) | | | |
| d. | | | | | |
| 10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited. Not available for sale to the public. | | | | | |
| 11. SUPPLEMENTARY NOTES Chemical toxic compounds, analytical studies | | | 12. SPONSORING MILITARY ACTIVITY | | |
| 13. ABSTRACT Bipotentiometric titrations of various polynuclear aromatic hydrocarbons, benzenes substituted with electron-donating groups, and π -excessive heteroaromatics in trifluoroacetic acid - dichloromethane with lead (IV) or cobalt (III) acetate solution resulted in novel titration curves. Each reagent increment usually resulted in the formation of a potential "saw tooth," indicating formation and decay of reversible redox couples; the final titration curves had one or more potential minima regions before the end-point. In almost all instances the titration curve for a given aromatic compound is characteristic, somewhat in the manner of a spectrophotometric curve. | | | | | |
| 14. KEYWORDS <div style="display: flex; justify-content: space-between;"> <div> Bipotentiometry Trifluoroacetic acid Aromatic compounds Radical cations </div> <div> Lead tetraacetate Oxidation Depolarization </div> </div> | | | | | |

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Analytical Chemistry Branch

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Task 1B562602AD1002

DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Chemical Laboratory
Edgewood Arsenal, Maryland 21010

FOREWORD

The work described in this report was authorized under Task 1B562602AD1002, Chemical Toxic Compounds, Analytical Studies. The work was started in October 1969 and completed in June 1970.

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DIGEST

Bipotentiometric titrations of various polynuclear aromatic hydrocarbons, benzenes substituted with electron-donating groups, and π -excessive heteroaromatics in trifluoroacetic acid - dichloromethane with lead (IV) or cobalt (III) acetate solution resulted in novel titration curves. Each reagent increment usually resulted in the formation of a potential "saw tooth," indicating formation and decay of reversible redox couples; the final titration curves had one or more potential minima regions before the end-point. In almost all instances the titration curve for a given aromatic compound is characteristic, somewhat in the manner of a spectrophotometric curve.

BIPOTENTIOMETRY IN ORGANIC REDOX SYSTEMS

PART I. OXIDATION OF AROMATIC COMPOUNDS IN TRIFLUOROACETIC ACID

HARVEY W. YUROW AND SAMUEL SASS

Research Laboratories, Edgewood Arsenal, Md. 21010 (U.S.A.)

(Received June 22nd, 1970)

Intense colors have been observed in spot-test reactions of polynuclear aromatic hydrocarbons oxidized with lead(IV) acetate in trifluoroacetic acid (TFA)¹. By analogy to electrochemical oxidations, it was postulated that these colors involved radical cation species^{2,3}. If these species are sufficiently stable, then they might form electrochemically reversible redox couples that can be detected by means of bipotentiometry. This technique, which has been applied almost exclusively to inorganic systems⁴, makes use of a pair of platinum electrodes polarized with several microamperes of direct current. If an electrochemically irreversible substrate is reacted with a reversible titrant, then the potential between the two electrodes (one polarized, the other depolarized) remains high during the titration but drops sharply in the vicinity of the end-point when both electrodes are depolarized. An electrochemically reversible redox couple is one that can depolarize electrodes, because the relatively rapid rate of electron transfer maintains equilibrium at the electrodes.

Organic bipotentiometry, especially that for aromatic compounds, can differ from the above in that during the titration of irreversible substrate with irreversible oxidant, intermediate reversible redox species of short but appreciable half-lives are formed. This is especially true in a solvent medium of low basicity such as TFA.

EXPERIMENTAL

Reagents

Lead(IV) acetate was prepared from red lead(IV) oxide⁵, while cobalt(III) acetate was readily obtained from cobalt(II) acetate and lead(IV) acetate⁶ in TFA. The solution of the lead(IV) salt, 0.1 *N* in TFA, lost about 1% titer per day, and the solid material slowly decomposed on standing, so that frequent standardization was required.

The oxidants were standardized with bromohydroquinone (K & E Labs), recrystallized from water and standardized with dichromate in aqueous solution using diphenylamine-sulfonate indicator. The standardization of oxidant, 0.1 *N* in TFA was done potentiometrically in a 1:1 (v/v) mixture of TFA (Eastman) and dichloromethane containing 0.01 *M* silver trifluoroacetate.

Aromatic compounds investigated were commercially available samples in the purest grades available. Stock solutions $5.0 \cdot 10^{-3}$ *M* in dichloromethane were prepared fresh every other day.

Equipment

Potential measurements were made with a Beckman expanded-scale pH meter connected to a Sargent model MR recorder. Electrodes were made with 1-mm diameter silver or platinum wire. Direct current was provided from a step-down transformer with a selenium rectifier (2.2 V) and a series resistance (0.3 M Ω).

Procedure

The bipotentiometric titration was performed in a 5-ml beaker with a microbar stirrer and a two-hole aluminum foil cap to minimize evaporation of the solvent mixture which was 1 ml of TFA, 0.50 ml of stock solution, and 0.5 ml of dichloromethane. The substrate concentration was $1.25 \cdot 10^{-3} M$. Air was not excluded from the system, which was run at ambient temperature. The electrodes were 5-cm lengths of platinum wire mounted in a polyethylene cap, spaced 1 mm apart and polarized with 7 μA of applied direct current. Oxidant, 0.10 N in TFA, was introduced with a 2-ml Gilmont microburet in increments of 5 μl , at 15-sec intervals. The chart speed was 0.5 in min^{-1} .

For reasons of economy, the TFA was recovered from the expended solvent mixture by a simple fractionation.

RESULTS AND DISCUSSION

Preliminary experiments

Initial additions of oxidant to an aromatic substrate resulted in an almost instantaneous change in potential (ΔE) between the polarized electrodes, followed

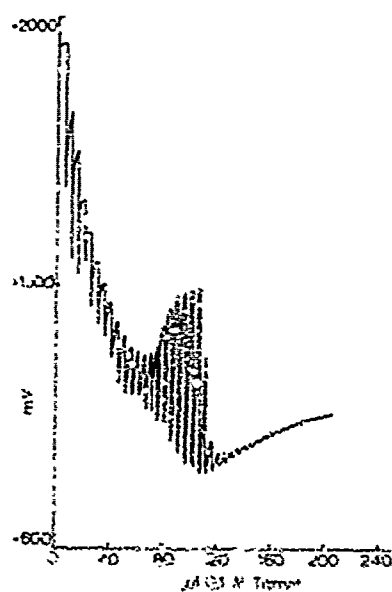


Fig. 3. Bipotentiometric titration of 1-phenylnaphthalene with lead(IV) acetate, a type I BM curve.

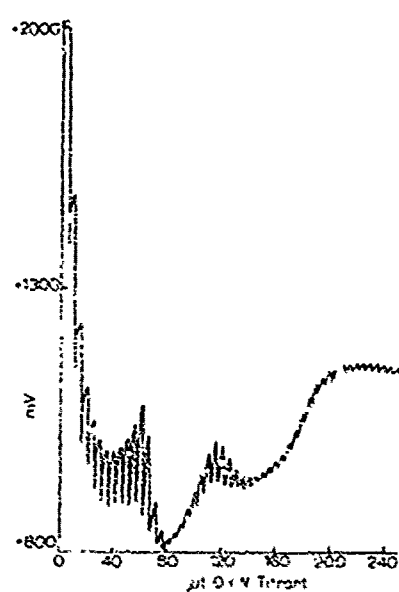


Fig. 2. Bipotentiometric titration of phenanthrene with cobalt(III) acetate, a type III S curve.

by "decay" of potential to a new value. This increment was usually of the "saw-tooth" type. These increments went to make up titration curves that had one or more potential minima regions before the end-point (see Figs. 1-4).

The shape and magnitude of the increments as well as the shape of the titration curve for a given substrate were quite sensitive to a variety of parameters, some of which are considered in detail in this paper. The four major parameters were: co-solvent, oxidant, applied current (more specifically current density) and delay time between additions. Because of the low solubility of many aromatics in TFA, a relatively inert co-solvent was required. Dichloromethane was found to be satisfactory and had the added advantage that TFA could be readily recovered by fractionation from mixtures with it. Other polyhalogen alkanes could be substituted with noticeable change in increment shape. Benzene was too reactive to be a suitable solvent.

It was noted that lead(IV) and cobalt(III) oxidants gave only small potential drops in blank titrations, indicating a low degree of electrochemical reversibility and allowing successful titrations to be made. With the various substrates, these two reagents were found to differ in two important ways. With almost all of the compounds tested, cobalt(III), a 1-equivalent oxidant, gave larger ΔE values than lead(IV), a 2-equivalent oxidant. This effect was magnified in very dilute solution (substrate $1.25 \cdot 10^{-4} M$). Also, markedly different type curves were often given by both oxidants with a given substrate. Manganese(III) behaved similarly to cobalt(III), while thallium(III) acetate reacted only with the most reactive substrates.

The current applied was $7 \mu A$ ($2.1 V/0.3 M\Omega$), but because of high solution resistance, the actual value as measured with a microammeter was only about half.

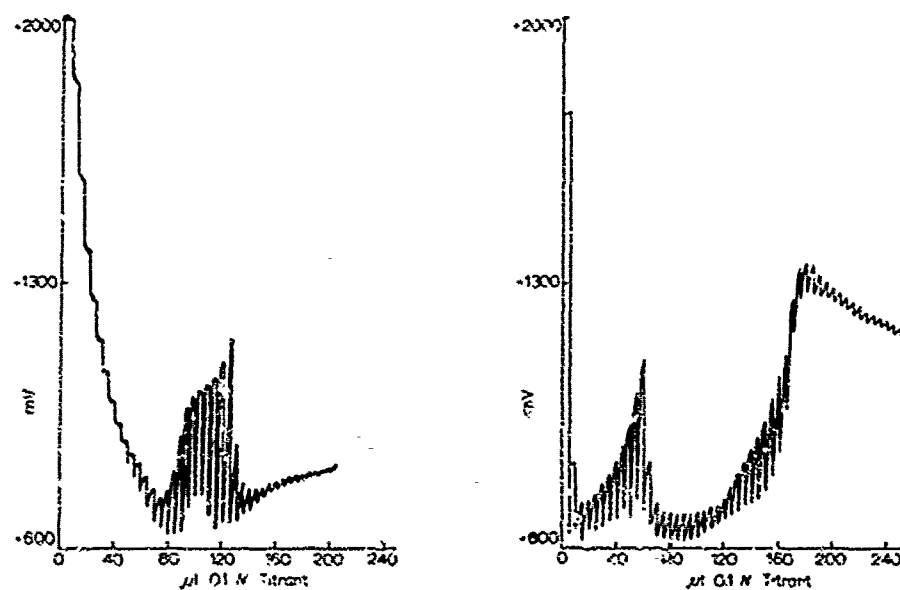


Fig. 1. Bipotentiometric titration of phenanthrene with lead(IV) acetate, a type I AS curve.

Fig. 4. Bipotentiometric titration of 1,2,3,4-dibenzanthracene with cobalt(III) acetate, a type II AS curve.

TABLE I
CLASSIFICATION OF BIPOTENTIOMETRIC CURVES FOR VARIOUS AROMATIC COMPOUNDS

| Class | Compound | Classification | |
|---------------------------------------|--------------------------|---------------------|------------------------|
| | | Lead(IV) acetate | Cobalt(III) acetate |
| I. Polynuclear aromatic hydrocarbons | 1. Linear | | |
| | Naphthalene | I AM | II BS |
| | Anthracene | II BS | I BS* |
| | Naphthacene | I BM | III M |
| | 2. Angular anthracene | | |
| | 1,2-Benzanthracene | II AS | II AS |
| | 1,2,3,4-Dibenzanthracene | I BS | II AS |
| | 1,2,5,6-Dibenzanthracene | I BS | II AS |
| | 3. Angular phenanthrene | | |
| | Phenanthrene | I AS | III S |
| | Chrysene | I BM | IV S |
| | 3,4-Benzophenanthrene | II AS | II AS |
| | 4. Condensed ring | | |
| | Triphenylene | I BS | I BS |
| | Pyrene | I BS | I BS |
| | 1,2-Benzopyrene | I BS | I BS |
| | 3,4-Benzopyrene | III M | III M |
| | Perylene | I BM | I BM |
| | 5. Polyaryl | | |
| | Biphenyl | I AS | I BS* |
| | p-Terphenyl | I BS* | I BS* |
| | 1,1-Binaphthyl | I BS | II AS* |
| | 2,2-Binaphthyl | II BS | II AS |
| | 1-Phenylnaphthalene | I BM* | III M |
| | 2-Phenylnaphthalene | I AM | I BS |
| | 9,10-Diphenylanthracene | II BM | II BM |
| | 6. Non-alternant | | |
| | Fluorene | I BS | I BM* |
| | Fluoranthene | I BM* | I BM* |
| | Acenaphthene | I BS | I BM* |
| | Acenaphthylene | I AS | I BM |
| | Azulene | I AS | I BM |
| | 7. Polyene | | |
| | cis-Stilbene | I AM | II AS* |
| | trans-Stilbene | I AS | II AM* |
| | 8. Miscellaneous | | |
| | Diphenylene | I BM* | I BM* |
| II. Substituted benzenes | 1. Ethers | | |
| | Anisole | I BS | I BS |
| | 2-Chloroanisole | II AS | I BS |
| | 3-Chloroanisole | I, I' defined | I BS |
| | 4-Chloroanisole | II AS* | I BS* |
| | 2. Phenols | | |
| | Phenol | I AM | I BS |
| | 2-Chlorophenol | I AM | I AM |
| | 3-Chlorophenol | I AM | I AS |
| | 4-Chlorophenol | I AM | II BM |
| | 3. Amines | | |
| | Aniline | III-defined | III-defined |
| | 2-Chloroaniline | I AS | I BM |
| | 3-Chloroaniline | III-defined | III-defined |
| | 4-Chloroaniline | III-defined | III-defined |
| | Diphenylamine | I BM | I BM |
| III. π -Excessive heteroaromatics | Thiophene | I BM | III-defined |
| | Carbazole | I BM | I BM |
| | Phenothiazine | II AM | II AM |
| | Phenothioxin | I BM | II BM |
| | Phenoxazine | II AM | II AM |

* Relatively large ΔE increments.

This value was just sufficient, under experimental conditions with the majority of compounds (anisoles and phenols required $3.5 \mu\text{A}$), to bring the pH meter needle on scale with the asymmetry control. Consequently, the scale included a $1,400 \text{ mV}$ span between about $+600$ and $+2000 \text{ mV}$. Smaller applied currents changed the ΔV values somewhat but not the shape of the titration curves. With the same current ($7 \mu\text{A}$ and a larger ballast load, $49 \text{ V}/7 \text{ M}\Omega$) less well-defined curves were obtained than with the above. A 15-sec interval between titration additions and a chart speed of 0.5 in min^{-1} were found to be optimal for the qualitative comparison of the compounds studied; but for quantitative studies, other values of current density, ballast load and interval between additions might be more suitable.

Other parameters that were found to affect the shape of increments included: (a) presence of added bases, such as water (1%) in the solvent mixture, that combined with reactive intermediates, and (b) rapidity of reagent addition and stirring, which influenced ΔV values.

Finally, it should be mentioned that inclusion of a third (reference) electrode¹, consisting of a silver wire dipping into the titration mixture containing 0.01 M silver trifluoroacetate, gave different curves when reference and anode or reference and cathode potential difference was measured.

Classification of titration curves

Well-defined titration curves were considered to be those with an end-point break and, preferably, one or more potential minima. Certain compounds (e.g. aniline, and the π -deficient heteroaromatics—acridine, phenazine, and phenanthridine) gave "saw-tooth" increments but poorly defined curves which lacked both potential minima and end-points.

Classification was based upon titration of fresh stock solutions of assumed relatively pure compounds. Solutions used over more than 1–2 days often gave significantly different results.

The curves for representative compounds of different classes of aromatic compounds with lead(IV) and cobalt(III) are classified in Table I. The curves, representative examples of which are given in Figs. 1–4, are classified on the following basis.

1. Whether the curve had I, II, III, etc. potential minima before the end-point. Potential minima were "troughs" in the titration curves formed by drawing a line connecting increments at their upper tips. With lead(IV) titrant almost all substrates gave a curve having a slight rise after the end-point, which for the purpose of classification was not considered a true potential minimum.

2. Whether the minimum potential was above (A) or below (B), that for the end-point for type I curves; or whether the first minimum was above (A) or below (B), that for the second for type II curves. Type III and IV curves were sufficiently rare that no further subdivision of this type was made.

3. Whether the curve was made up exclusively of "saw-tooth" increments (S) or included a significant number of mixed type increments (M). "Saw-tooth" increments were those where the internal angle of the "saw-tooth" was less than 90° . Other increments were often encountered with angles between 90° and ca. 135° . Occasionally inverse increments resulted.

This classification (Table I) leads to the observation that for condensed poly-

nuclear aromatic hydrocarbons and four out of five π -excessive heteroaromatics studied, both oxidants gave curves of the same class type.

Quantitative relationships

Quantitative relationships among the various curves were not studied in any detail in this investigation but would include magnitude of potential drop (ΔE), decay rates of reversible redox couples, and stoichiometry at potential minima and end-points. For these parameters, it would be necessary to control fairly closely such factors as temperature and speed of addition. However, it is noteworthy that under the experimental conditions used, a number of biaryls and *p*-substituted anisoles gave relatively large ΔE values. Decay rates varied considerably (ca. 0.1–1 min half-lives), not only from compound to compound but even in various positions of a given titration curve. In many instances, increments in the ascending portion of a curve decayed more rapidly than those in the descending portion. Potential minima often did not correspond to integral oxidation equivalents, possibly indicating concurrent rather than sequential oxidation. For many of the curves, end-points were relatively gradual and non-stoichiometric, which is probably partly due to the non-equilibrium conditions employed. Further, reaction of substrate with oxygen in the air was observed with reactive hydrocarbons such as perylene or rubrene.

Almost all of the compounds examined gave vivid color transitions during the titrations. In a number of instances these changes corresponded to sharp changes in the bipotentiometric curves.

Oxidation mechanisms

For bipotentiometry and biamperometry electrochemically reversible redox couples are essential. In organic bipotentiometry in a relatively inert solvent, electrochemical reversibility and, consequently, the shape and size of the titration increments will depend essentially upon two equations:



Oxidations involving loss of an electron (eqn. (1)) are capable of being electrochemically reversible, while loss by substrate of a hydrogen atom (except OH or NH_2 , or a hydride ion generally renders them irreversible. Further, if the rate of dimerization of the radical cation is rapid (relatively unstable radical cation) compared to the rate of initial electron transfer then reaction (1) will be rendered irreversible.

Electrochemical and/or chemical evidence indicates that for polynuclear aromatic hydrocarbons⁸, heteroaromatics⁹, and aromatic ethers⁹, initial oxidation gives the radical cations $\text{Ar}^{\cdot+}$ and $\text{Ar}-\text{O}^{\cdot+}\text{R}$, respectively, while phenols^{9,10} give $\text{Ar}^{\cdot+}$. Amines oxidized electrochemically give $\text{Ar}-\text{NH}_2^{\cdot+}$, and chemical oxidation produces $\text{Ar}-\text{NH}^{2+}$. These radical cations differ widely in instability with respect to dimerization. Relative stabilities can be estimated by Highest Filled Molecular Orbital calculations⁸. Radical cations from π -deficient heteroaromatics and anilines are particularly unstable⁹. In the current investigation, it was found that all of the examined polynuclear aromatic hydrocarbons, phenols (with cobalt(III) only), and aromatic

ethers gave well-defined titration curves, indicating that even the most unstable of these radical cations or cations were sufficiently stable to cause depolarization, while several anilines tested gave poorly defined curves (the *o*-chloro compound being an exception).

One may speculate on the relative size of the potential drops¹². Since the titration solutions were stirred, mass transfer rates were relatively rapid and, as was observed, radical cation half-lives were of comparable duration to measurement times. Consequently, the electron transfer rate apparently controls the magnitude of ΔV . Since very little information is available on organic electron transfer coefficients, meaningful discussion is not yet possible.

While the first step in the above oxidations is relatively straightforward, subsequent loss of electrons is more complicated. Stoichiometry for organic bipotentiometry indicated that two or more equivalents of oxidant were often involved. Possible reactions for polynuclear aromatic hydrocarbons include oxidation of dimer to radical cation $Ar-Ar^{\cdot+}$ or to $Ar-Ar^{2+}$ or oxidation of radical cation to cation Ar^{2+13} , reactions which may be concurrent or sequential. Further information could be obtained by coupling bipotentiometry with such techniques as spectrophotometry, electron spin resonance, or cyclic sweep voltammetry.

SUMMARY

Bipotentiometric titrations of various polynuclear aromatic hydrocarbons, benzenes substituted with electron-donating groups, and π -excessive heteroaromatics in trifluoroacetic acid-dichloromethane with lead(IV) or cobalt(III) acetate solution resulted in novel titration curves. Optimum qualitative results were obtained with a 15-sec delay between additions of titrant. Each reagent increment usually resulted in the formation of a potential "saw-tooth", indicating formation and decay of reversible redox couples; the final titration curves had one or more potential minima regions before the end-point. Because of considerable differences in number, reversibility and stability of oxidation intermediates, no two aromatics of those tested gave identical curves. However, sufficient similarities existed to permit a system of curve classification and some degree of correlation. The technique is at present essentially a qualitative one. In almost all instances the titration curve for a given aromatic compound is characteristic, somewhat in the manner of a spectrophotometric curve.

RÉSUMÉ

Une étude est effectuée sur les titrages bipotentométriques de divers hydrocarbures aromatiques polynucléaires, de benzènes substitués et de composés hétéroaromatiques, dans le milieu acide trifluoroacétique-dichlorométhane, à l'aide de solutions d'acétate de plomb(IV) et de cobalt(III). Cette technique est actuellement essentiellement qualitative. Dans presque chaque cas, la courbe de titrage est caractéristique pour un composé aromatique donné, une peu à la manière d'une courbe spectrophotométrique.

ZUSAMMENFASSUNG

Verschiedene mehrkernige aromatische Kohlenwasserstoffe, mit Elektronen-

donor-Gruppen substituierte Benzole und π -elektronenreiche Heteroaromaten wurden in Trifluoressigsäure-Dichlormethan mit Blei(IV)- oder Kobalt(III)-acetat-Lösung bipotentiometrisch titriert. Es ergaben sich neuartige Titrationskurven. Optimale qualitative Ergebnisse wurden erhalten, wenn das Titrationsmittel in Abständen von 15 sec zugegeben wurde. Jede Reagenzzugabe führte normalerweise zu einer sägezahnförmigen Potentialveränderung, die Bildung und Zerfall reversibler Redoxpaare anzeigte. Die schliesslich erhaltenen Titrationskurven hatten vor dem Endpunkt einen oder mehrere Bereiche mit Potentialminima. Wegen der erheblichen Unterschiede in der Anzahl, Reversibilität und Stabilität der Oxidationszwischenstufen waren unter den untersuchten Aromaten keine mit identischen Titrationskurven. Dagegen waren genügend Ähnlichkeiten vorhanden, die ein System der Kurvenklassifizierung erlaubten und in gewissem Grade Beziehungen erkennen liessen. Das Verfahren ist gegenwärtig im wesentlichen für qualitative Zwecke anwendbar. Bei fast allen Beispielen ist die Titrationskurve für eine gegebene aromatische Verbindung charakteristisch, etwa in der Art einer spektrophotometrischen Kurve.

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